L. RAMQVIST

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ALMQVIST & WIKSELLS BOKTRYCKERI AB

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Preparation, properties and electronic structure of refractory carbides and related compounds

INAUGURAL DISSERTATION

BY

LARS RAMQVIST

FIL. LIC., V-DALA

By due permission of the Faculty of Science
of the University of Uppsala, to be publicly
discussed in the lecture hall of the Institute of Chemistry,
March 28, 1969, at 10 a.m.,
for the degree of Doctor of Philosophy.
In addition to this review the
papers numbered 2, 3, 4, 4a, 5, 6, 7, 8, 9 and 10 in the list
of references will be publicly discussed

UPPSALA 1969

ALMQVIST & WIKSELLS BOKTRYCKERI AB

PREPARATION, PROPERTIES AND ELECTRONIC STRUCTURE OF REFRACTORY CARBIDES AND RELATED COMPOUNDS

LARS RAMQVIST*

INTRODUCTION

Refractory carbides, i.e. transition-metal carbides of Groups 4b (Ti, Zr, Hf), 5b (V, Nb, Ta) and 6b (Cr, Mo, W) have successfully been used in the hard metal industry for many decades due to their high hardness, high melting points and strength at elevated temperatures. Although there has been great interest in studying the properties of the carbides, surprisingly few accurate data have been reported, especially for the variation of properties with carbon content. When earlier data exist, they are often wrong or misleading. In the light of present technology it is evident that many earlier reported data, often accepted and referred to in handbooks, were obtained from impure and poorly defined carbides. The most serious sources of error are due to dissolved oxygen and nitrogen and to varying carbon content. Therefore many physical and chemical properties must be remeasured with special attention to the use of pure and well defined carbides.

Thanks to Hägg [1], the crystal structure of carbides and other interstitial phases was elucidated at a relatively early stage of the research within this field. The simple atomic arrangement of Groups 4b and 5b metal carbides and their unusual physical and chemical properties have led to the development of numerous theories and models for the bonding in carbides. Measurements directly relating to the electronic structure are, however, generally missing in these papers, of which the most quoted and recently published ones will be further discussed in the present paper.

The present paper reviews and correlates a series of recent investigations on the refractory carbides of Groups 4b, 5b and 6b. The main body of these have been performed by the present author and coworkers during 1963–1968. The earliest investigations dealt with the preparation of carbides by means of hot pressing [2, 3]. The hot-pressed carbide discs were used for a comprehensive experimental investigation on the wetting of carbides by liquid copper, nickel, cobalt and iron [4]. This "outer bonding" of the carbides is of fundamental importance for the sintering process and for the properties of hard metals. As a complement to these studies, we also investigated the "inner bonding", i.e. the electronic structure of carbides and to a certain extent its significance for the physical and chemical properties. We have measured the x-ray absorption and emission [5, 6] and electron spectra [7, 8] of carbides and related compounds and correlated them to give a model of the electronic structure.

This combination of methods gives an experimentally based picture or model of the electronic structure of carbides from the core electron levels up to the band structure at the Fermi level. This model has furthermore been successfully correlated with recent quantum mechanical (Augmented Plane Wave) calculations. We have thus obtained a picture of the electronic structure which enables us to correlate physical and chemical properties of the carbides with their electronic structure. Since property data often have shown to be wrong and missleading, however, we remeasured carefully some important physical properties of carbides. The variation of lattice parameter and hardness with carbon content of Group 4b and 5b metal carbides was studied and used for a qualitative correlation with electronic structure [9, 10]. This paper extends the correlation between various recently measured properties and the electronic structure.

The investigations presented in this paper represent an introductory study of the electronic structure and its significance for the physical and chemical properties of refractory compounds. Although we have investigated, in addition to carbides, TiB_2, TiN, TiO and TiO_2, much works still remains to be done on the related phases of Groups 4b, 5b and 6b. Beside further studies of the electronic structure of refractory phases, their physical and chemical properties must be much more accurately

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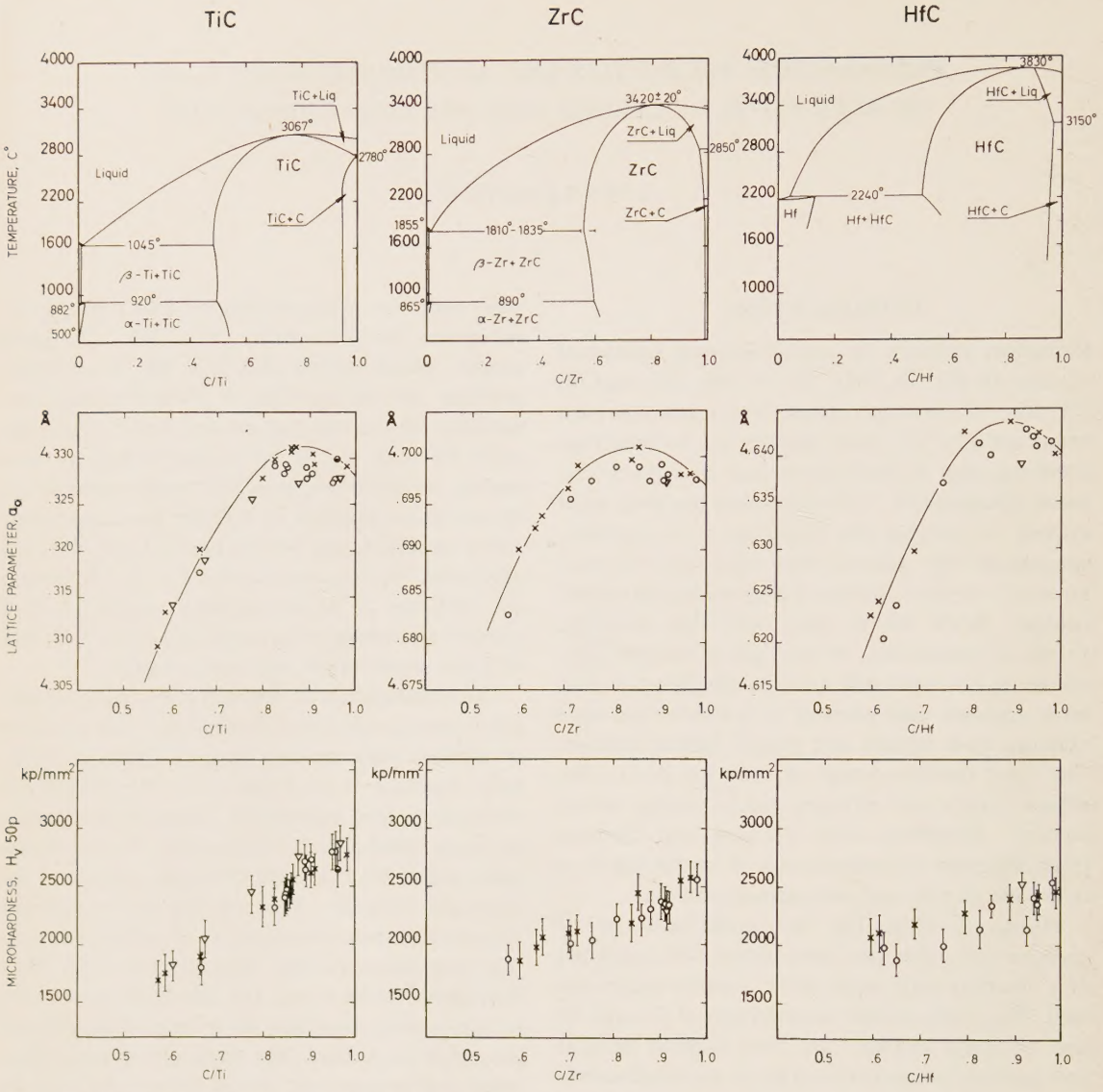

Fig. 1. Homogeneity ranges of Group 4b carbides and variations of lattice parameter and hardness with composition (atom ratio C/Me) of these carbides prepared by arc melting (×), gas carburization (○), hot pressing (▽) and single crystal growth (◒).

measured than they generally are so far. Present technology, however, permits this to be fulfilled and to result in a consistent and useful knowledge of refractory materials.

GENERAL FEATURES OF TRANSITION-METAL–CARBON PHASE DIAGRAMS. PHYSICAL AND CHEMICAL PROPERTIES OF CARBIDES

Phase diagrams

The phase diagrams of Group 4b and 5b metal carbides are shown in Figs. 1 and 2. These diagrams are shown to give the reader a general feature of the homogeneity ranges of the carbides. Only well characterized phases are shown, even if other phases may exist.

The transition metals of Groups 4b, 5b and 6b combine with carbon and give phases with simple atomic arrangements. The MeC-type carbides of Groups 4b and 5b exhibit the cubic face centered (NaCl, B1) structure and wide homogeneity ranges. It is noteworthy, however, that the VC phase has a remarkably small homogeneity range with an upper limit around $VC_{0.88}$. This phase is in many respects

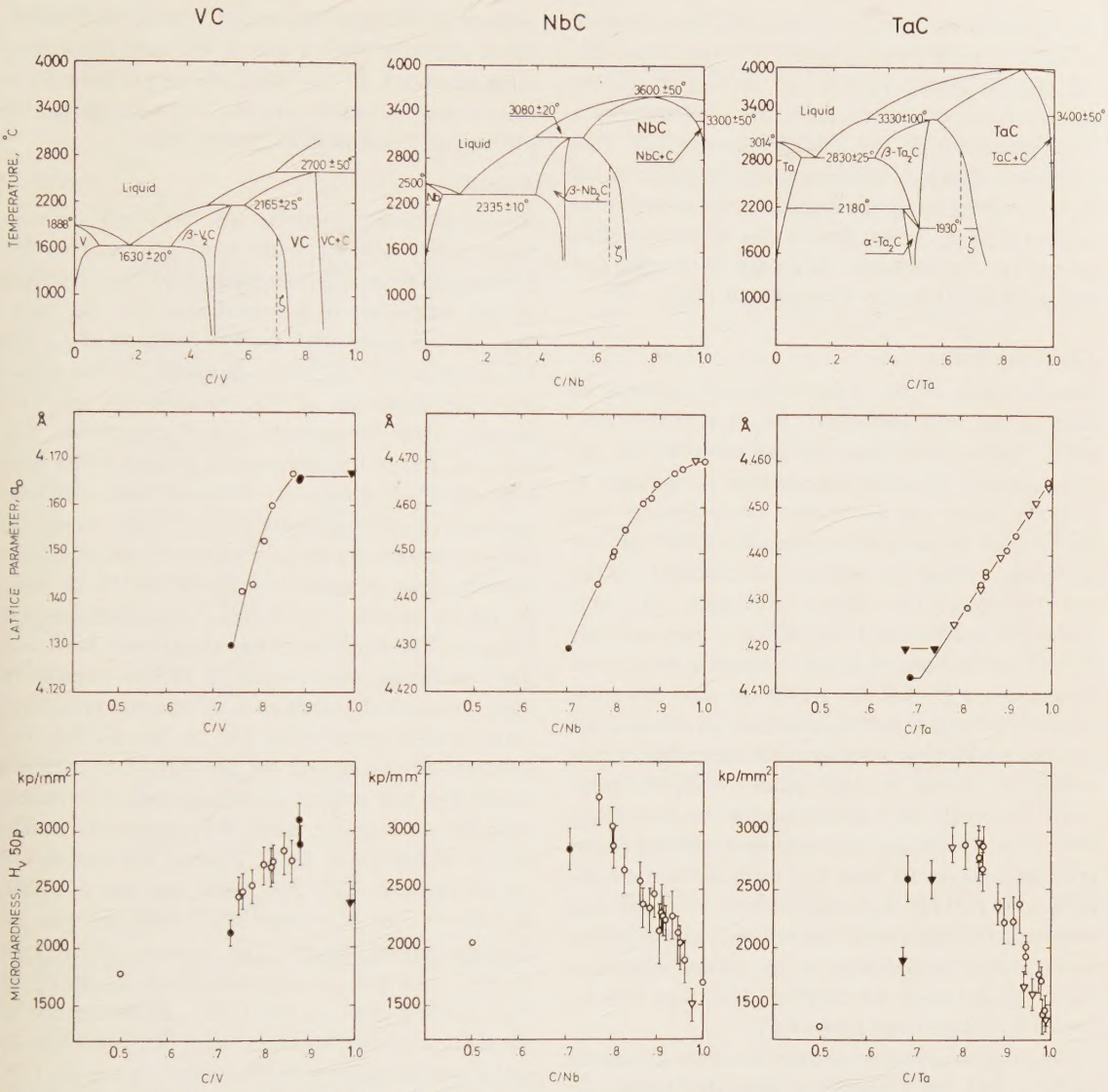

Fig. 2. Homogeneity ranges of Group 5b cubic carbides and variations of lattice parameter and hardness with composition (atom ratio C/Me) of these carbides prepared by gas carburization (○) and hot pressing (▽). Black symbols represent two phases. In addition the homogeneity ranges of the Me_2C and ζ phases are shown.

different from the NbC and TaC phases as will be pointed out further below. Furthermore, it is interesting to note that recent investigations by Venables [11] on the V-C system point to an ordered compound V_6C_5 which has no counterparts in the Nb-C and Ta-C systems.

Group 5b carbides also show a Me_2C type with a hexagonal structure ($L'3$). Other structures of the Me_2C phases are discussed by Storms [12]. Furthermore, the ζ phase, still with uncertain crystal structure [12], can be found at the lower MeC-phase limits in the carbide systems containing a Group 5b metal.

Group 6b carbides have somewhat more complicated crystal structures. For example WC and Mo_2C have a hexagonal D^1_{3h} and an orthorhombic D^{14}_{2h} structure, respectively. However, even the most complex one, the Cr_3C_2 orthorhombic structure D^{16}_{2h} – Pbnm (Pnma) [12], is still a relatively simple structure. Since most of the present author's work concerns the cubic 4b and 5b carbide phases, only the industrially important Cr_3C_2, Mo_2C and WC phases from Group 6b will be further discussed in this paper.

The carbides have the highest melting points of any

known material. In spite of the difficulties involved in measuring the melting points it is now clear that the melting point maxima do not occur at the stoichiometric compositions of the carbides. For a good discussion we can refer to Storms [12]. That the stoichiometric carbide always is the one with the highest melting point, the highest hardness and so on is still stated in current handbooks which are often referred to, for example the books by Kieffer and Benesovsky [13] and by Goldschmidt [14].

Lattice parameter

Measurements of the x-ray diffraction patterns of carbides are very important. Beside a lattice-parameter determination and a phase identification the homogeneity of the carbide sample is revealed. If properly used the parameter measurements can furthermore be used advantageously as an indirect analysing method for carbon and dissolved oxygen and nitrogen. The lattice parameters of cubic Group 4b and 5b metal carbides have been carefully studied as functions of carbon content in two of our investigations [9, 10], for which the data are summarized in Table I. In these papers it was shown that the lattice parameter increases with increasing carbon content of Group 5b MeC phases while the parameter curve exhibits a maximum for the carbides of Group 4b. This is in close agreement with the recent investigations on TiC and ZrC collected in the book by Storms [12] but in sharp contrast to earlier data referred to in handbooks like refs. [13] and [14]. The occurrence of a maximum in the lattice parameter curve for a Group 4b carbide, TiC, was first reported by Norton and Lewis [15].

Oxygen and nitrogen increase the lattice parameter of NbC and TaC, while the effect for Group 4b carbides is inverse. According to Storms [12], dissolved gases also can raise the lattice parameter of VC. However, this must still be considered somewhat unclear. As shown in ref. [10] $\gtrsim 1.5$ wt.% dissolved gases in TiC lower the lattice parameter by ~ 0.015 Å. Even very small amounts of dissolved gases, in the region of $\gtrsim 0.1$ wt.%, were shown to influence the lattice parameter values appreciably. In addition, dissolved gases, if more than 0.2–0.3 wt.%, cause the maxima in the lattice parameter curves to disappear and thus to give an incorrect picture of the variation of lattice parameter with carbon content. The lattice-parameter function is one of many examples of the serious influence of dissolved gases.

The variation of lattice parameter with carbon content of Groups 4b and 5b metal carbides [9, 10] is shown in Figs. 1 and 2. We have not studied these functions for the Me_2C phases of Group 5b or for the carbides of Group 6b. The x-ray diffraction method used was described in ref. [9].

Hardness

In industry the property of refractory carbides most widely utilized is the hardness, but very few investigations on the hardness have been reported in the literature. It is remarkable that the variation of hardness with carbon content of Group 5b carbides has not been accurately studied at all, with the exception of the investigation on TaC recently made by Santoro [16]. In handbooks, e.g. ref. [14], and in the literature in general it has been concluded, obviously on a vague base, that the hardness of cubic carbides increases with increasing carbon content. As we have shown, however, in two investigations on cubic Group 4b and 5b carbides [9, 10] the variation of hardness with composition is irregular. The hardness of the 5b carbides NbC and TaC decreases with increasing carbon content in their homogeneity ranges, i.e. in essential agreement with the result reported for TaC by Santoro [16]. The hardness maximum and the declination of hardness found at a low carbon content in these two phases were shown to be the result of intragranular precipitation of the softer Me_2C phases. The hardness of the 4b carbides TiC, ZrC, HfC and also of the 5b carbide VC, on the other hand, increases with increasing carbon content. The variation of hardness of NbC_x and TaC_x is substantial and, as shown by Figs. 1 and 2, $NbC_{0.75}$ and $TaC_{0.75}$ are the hardest of the metal carbides, together with $VC_{0.88}$. Group 4b carbides, referred to in the literature, see e.g. ref. [13], as the hardest carbides, are less hard, provided they are free from dissolved gases. The hardness, especially that of Group 4b carbides [10], was shown to be heavily affected by dissolved gases, a fact that together with the influence of the carbon content explains the enormous divergency in earlier reported hardness values. As reported in ref. [10] 1 wt.% dissolved oxygen and nitrogen will raise the hardness by 500 kp/mm² (50 p load). Hardness data of the carbides from refs. [9, 10] are summarized in Table I and in Figs. 1 and 2. The method used was described in ref. [9].

Heat of formation

Heat of formation is a very useful and important theoretical and thermodynamical quantity. It is the

Table I. *Properties of transition-metal carbides of Groups 4b, 5b and 6b*

Carbide[a]	Lattice parameter a_0 Å	Micro-hardness[b] $H_{v\,50p}$ kp/mm²	Resis-tivity[c] ϱ 20°C $\mu\Omega$ cm	Heat of formation $-\Delta H_{298°K}$ kJ/mole	Wetting by liquid metals[d]							
					Cu (1100°C)		Ni (1380°C)		Co (1420°C)		Fe (1490°C)	
					$\theta°$	Wa erg/cm²	$\theta°$	Wa erg/cm²	$\theta°$	Wa erg/cm²	$\theta°$	Wa erg/cm²
Group 4b												
TiC	4.3278±0.0002	2800	68	184±2	112	790	23	3475	25	3640	28	3570
$TiC_{0.7}$	4.3220±0.0001	1950	140		88	1315						
ZrC	4.6976±0.0001	2600	42	197±3	127	505	24	3460	36	3460	45	3245
$ZrC_{0.7}$	4.6966±0.0001	2000	120									
HfC	4.6402±0.0001	2500	37	209±2	134	390	23	3475	40	3380	45	3245
$HfC_{0.7}$	4.6328±0.0001	2000	90									
Group 5b												
$VC_{0.88}$	4.1656±0.0002	3000	76	103±3	50	2085	17	3540	13	3770	20	3685
$VC_{0.7}$	4.1296±0.0002	2100	155									
NbC	4.4702±0.0001	1650	40	140±3	70	1675	18	3530	14	3760	25	3620
$NbC_{0.7}$	4.4295±0.0002	3000	165									
TaC	4.4555±0.0002	1420	17	143±3	78	1535	16	3550	13	3770	23	3650
$TaC_{0.7}$	4.4135±0.0003	3000	155									
V_2C	2.9034±0.0001 4.5794±0.0004	1770	114	69±3								
Nb_2C	3.1167±0.0003 4.9635±0.0005	2050	54	97±3								
Ta_2C	3.1075±0.0002 4.9499±0.0007	1330	49	104±4								
Group 6b												
Cr_3C_2	5.5274±0.0003 2.8289±0.0001 11.4838±0.0007	2140	75	23±5	47	2135	0	3620	0	3820	0	3800
Mo_2C	4.7306±0.0006 6.0297±0.0006 5.2010±0.0006	1530	71	23±2	18	2480	0	3620	0	3820	0	3800
WC	2.9060±0.0001 2.8371±0.0002	2350	19	40±2	20	2465	0	3620	0	3820	0	3800

[a] MeC represents a phase with maximum carbon content.
[b] The accuracy is ±5–8%.
[c] The accuracy is ±5%.
[d] The accuracy in wetting angles is ±2.5°.

chemical measure on the stability of the carbide phase and thus indirectly a measure of its bond strength. If one wishes to derive a measure of the bond strength from the heat of formation per mole, it is evident that this value must be corrected to the number of atoms in the mole. On this basis, the bond strength in a cubic-carbide phase is proportional to its heat of formation per mole divided by the number of atoms in the formula. We define the bond strength as heat of formation per N atoms, i.e.

$$-\frac{\Delta H_{298°K} \text{ per mole of } MeC_x}{1+x}$$

given in kJ per N atoms, where N = Avogadro's number.

A good survey of current values of the heats of formation is given by Storms [12]. These are summarized in Table I. The consensus regarding the heats of formation of stoichiometric carbides seems to be relatively good, with the exception of the carbides of Group 6b. Unfortunately, the nature of the variations of heats of formation with carbon content are not fully established, although several carbides have been investigated. Morozova *et al.* [17] have studied the variation of the heat of formation per mole with carbon content of TiC. They found an increase of the heat of formation, $-\Delta H_{298}$, from ~110 kJ/mole at $TiC_{0.5}$ to ~230 kJ/mole at $TiC_{1.0}$. Although their values can be considered too high compared to recent values for TiC [12], the slope of their curve is interesting. This slope implies that also

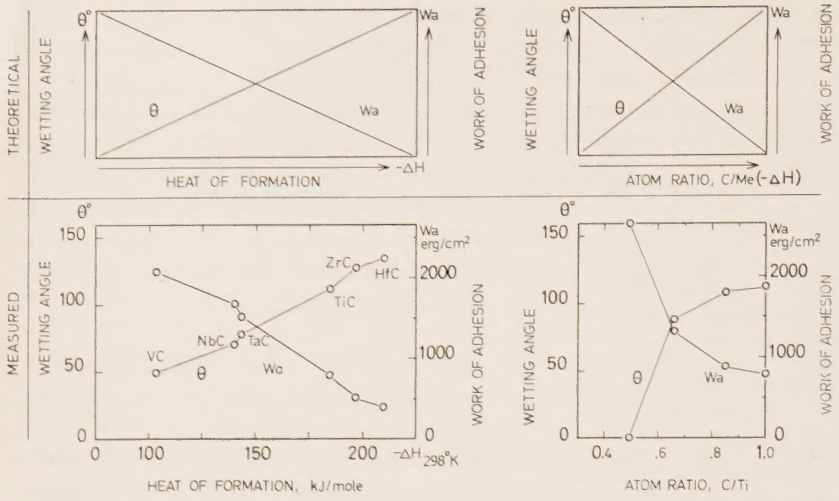

Fig. 3. Theoretically predicted and measured relationships between wetting angles and works of adhesion versus heats of formation of stoichiometric and non-stoichiometric cubic carbides of Groups 4b and 5b.

the bond strength increases with increasing carbon content.

A similar picture emerges from Mah's [18] study on the heat of formation of the ZrC phase. She reports a $-\Delta H_{298}$ value of 196.6 kJ/mole at $ZrC_{0.93}$ and $ZrC_{0.99}$ and a value of 138.5 kJ/mole at $ZrC_{0.71}$, i.e. the bond strength will increase when carbon atoms are added.

Huber *et al.* [19] have investigated on the variation of the heat of formation in the NbC phase. Their results indicate a decrease in the $-\Delta H_{298}$ value per N atoms from 71.6 kJ at $NbC_{0.8}$ to 70.9 kJ at $NbC_{1.0}$ [8]. Similar results are given for the TaC phase by Huber *et al.* [20]. The heat of formation per mole increases from 136.5 kJ at $TaC_{0.9}$ to 142.6 kJ at $TaC_{1.0}$, i.e. the value per N atoms decreases from 71.8 kJ to 71.3 kJ, respectively. At low carbon contents, i.e. at $NbC_{<0.8}$ and $TaC_{<0.8}$, low $-\Delta H_{298}$ values are given in refs. [19, 20], probably too low, due to interactions from the Me_2C phases.

For the cubic VC phase Volkova and Gel'd [21] found the heat of formation to vary with carbon content in such a way that the $-\Delta H_{298}$ value per N atoms increases from 52.8 kJ at $VC_{0.75}$ to 55.9 kJ at $VC_{0.88}$ [8].

From the measurements cited above, which are the most accurate investigations reported in the literature so far, we conclude that the heat of formation per mole increases with increasing carbon content for the cubic carbides of Groups 4b and 5b. Group 4b carbides show the greatest change with composition and such a great change that the heat of formation per atom also increases with carbon content. For VC, NbC and TaC the value per atom is almost constant with varying carbon content. However, although the variations of the heats of formation per atom with carbon content in these phases are small, and may seem negligible, it is interesting to notice that the quoted measurements suggest that the heat of formation per atom and thus the bond strength increases in the VC phase but decreases with increasing carbon content in the NbC and TaC phases.

Wetting by liquid metals

Wetting or "outer bonding" of carbides is of fundamental importance for the liquid phase sintering process used in the hard metal industry. To obtain dense and homogeneous compacts with useful properties the liquid metal should totally wet the solid carbide phase. The bonding between the two phases, i.e. the work of adhesion, will then be of optimal strength. The wetting of stoichiometric, non-stoichiometric and mixed carbides of Groups 4b, 5b and 6b by liquid copper, nickel, cobalt and iron were studied in one of our investigations [4]. It was possible to establish a relationship between wetting angles or works of adhesion and heats of formation of the carbides. It was thus found that the work of adhesion decreases with increasing stability of the carbide, i.e. with increasing heat of formation ($-\Delta H_{298°K}$) of the carbide. This relationship, i.e. $\theta \propto -\Delta H_{298}$/mole, was found to hold also for the variation of wetting with composition of the carbide. However, very few measurements were made on non-stoichiometric and mixed carbides. Our statement "the more stable the carbide, the less the wetting", which is the opposite to the earlier often quoted rule by Livey and Murray [22], has been

further verified by Hodson and Parikh [23] in their investigation on the wetting of carbides by liquid Cr-base alloys and by Warren [24] in his investigation on the interaction between liquid platinum and some transition-metal carbides. Wetting data for carbides from ref. [4] are summarized in Table I and Fig. 3. The method and the equipments used were described in ref. [4]. Our technique was also used by Warren [25] in his investigation on the wetting of WC/TiC (50:50 wt.%) by Co, Ni, Fe and their alloys.

Resistivity

It is well known that the transition-metal carbides in many respects resemble the pure metals. The carbides are thus good conductors of heat and electricity. The electrical resistivity of a stoichiometric cubic carbide of Groups 4b and 5b is only 10–30 $\mu\Omega$ cm higher than that of the corresponding pure metal. In ref. [9] we have reported the resistivity of Group 5b carbides to increase with decreasing carbon content. The resistivity was measured potentiometrically and its variation with carbon content was found to be substantial; for TaC the resistivity increases ten times within the composition range. An increasing resistivity with decreasing carbon content was found also for the Group 4b carbides [10]. Although we have not reported any exact resistivity values for Group 4b carbides in ref. [10] we will in this paper give values estimated from our measurements and from literature data [26]. Resistivity values are summarized in Table I.

PREPARATION TECHNIQUES

The preparation is a very critical step for studies of transition-metal carbides. As is evident from the paragraphs above, pure and well defined carbides must be used in order to get useful and correct data. How pure and how well defined a carbide can be obtained depends on the starting materials and on the mode of preparation. Often a relatively large, dense, homogeneous and chemically well defined surface is needed for the test. This was the case for our investigations on wetting and x-ray and electron spectra. In the following sections we will give a brief summary of the different modes of preparation selected and used by us to obtain pure and homogeneous carbide test samples. For surveys of other possible ways to prepare carbides we can refer to the books by Storms [12] and Kieffer and Benesovsky [13].

Hot pressing

Hot pressing implies that a powder compact is heated to a temperature below the melting point of the material and that an external pressure is simultaneously applied to cause rapid sintering of the powder into a dense body.

The theories of hot pressing and the hot pressing of industrially important transition-metal carbides were studied in detail in two of our investigations [2, 3]. Furthermore, we have described a somewhat modified method in a later paper [9].

The hot-pressing method is very useful when aiming at big carbide bodies, for example in an industrial production, where the demands for purity and homogeneity at the same time are not especially accentuated.

The contamination from the die, in general made of graphite, is a clear disadvantage. A non-stoichiometric carbide will thus pick up additional carbon. Carbon gradients are likely to occur if a not completely stoichiometric carbide is the end result. Furthermore, the fine-grained powder used as starting material will undoubtedly contain adsorbed gases which will dissolve in the carbide during the hot-pressing procedure. Neither protective atmospheres nor vacuum are perfect solutions to this problem. Vacuum hot pressing, described in ref. [3], is a very attractive method for stoichiometric carbides but is unfortunately not suitable for non-stoichiometric ones, since the vacuum here generally causes loss of material and consequently composition gradients in the carbide. Pure and homogeneous carbides of Group 5b and 6b can be prepared by hot pressing if the method is used in the following manner [3, 9].

The carbon pick-up can be prevented by the use of BN as an intercontact material between the carbide and the graphite die and punches. It is important to grind carefully the specimens afterwards to ensure clean carbide bodies, i.e. only the core of the hot pressed sample is used. Group 4b carbides and especially non-stoichiometric ones are, however, more difficult to obtain perfect by the hot-pressing method, even if balanced vacuum annealings are added in order to get rid of dissolved gases [10]. Analyses show that it is very difficult to achieve a gas content less than 0.3 wt.% for non-stoichiometric Group 4b carbides, while for the carbides of Groups

5b and 6b the gas content can be kept around or below 0.1 wt.%. Technical data for hot pressing of carbides and related compounds and the properties of these specimens can be found in refs. [2], [3] an [9].

Gas carburization

The method implies a reaction at elevated temperatures between a metal and a carbon-containing atmosphere, for example methane. Since the diffusion of carbon in transition metals generally is slow [26], it is of fundamental importance to have thin metal bodies, preferably small diameter filaments. It was shown in two of our investigations [9, 10] that well defined carbides of Groups 4b and 5b can be produced by methane gas carburization of small diameter metal filaments. This method gives very pure carbides, since the contamination can be kept to a minimum. However, the gas pick-up may be a problem unless a very tight vacuum equipment is used. Analyses show a gas content in the region of 0.02 wt.% for Group 5b carbides and around 0.2 wt.% for Group 4b carbides.

The homogeneity of the carbide filaments was furthermore shown to be very good for the Group 5b carbides. Group 4b carbides, on the other hand, were more difficult to obtain homogeneous unless long reaction times were used. It was found that perfectly homogeneous HfC_x filaments were difficult to produce even when a reaction time of 15 hours was used [10]. The composition can readily be changed with high precision, which makes this preparation method especially valuable in studies on carbides with varying carbon contents. Data for gas carburization of Group 4b and 5b metals are summarized in refs. [9] and [10].

Arc melting

The high melting points of the carbides make it sometimes difficult to use the arc melting method. Even if the carbide can be melted, serious problems still remain. One is the homogeneity problem, i.e. the problem to get a completely uniform composition throughout the sample. This problem can, however, be partly solved by remeltings and/or long-time annealings under proper conditions. If the test volume is kept at a minimum or only fragments of bigger melts are used, the homogeneity may of course be improved. Another problem is to ensure a predetermined composition. The high temperatures involved often cause loss of material and at the end a composition is given where the carbon and metal evaporate concurrentally. A further disadvantage is the contamination from the electrode, often made of tungsten.

The arc-melting technique has been used for preparation of carbides in two of our investigations [7, 10]. It was found that the gas content can be kept at a very low level, i.e. 0.01–0.08 wt.%, depending on the carbon content. The arc melting technique is therefore, properly used, of great value in studies of intrinsic properties of carbides and related compounds. Data of interest are collected in ref. [10].

Single-crystal growth

Single crystals would be of great value for an accurate knowledge about the intrinsic physical properties of carbides and the influences of dissolved gases, carbon content and grain boundaries on these properties. However, with present technology the only crystals readily available are titanium carbide grown by the Verneuil process. Attempts to modify and utilize this process for other carbides are being made together with tests on the liquid metal solution growth of crystals, see for instance ref. [27].

A TiC single crystal has been used in one of our investigations as a reference material [10]. Our results have furthermore been compared with literature data on TiC single crystals. Analyses show that the gas content in perfectly grown TiC_x single crystals is less than 0.02 wt.% [10, 28]. Without doubt it can be established that a homogeneous single crystal is the most perfect sample. By having the single crystals as reference material other preparation methods can thus be evaluated and the most reliable ones can be selected and used.

Analyses

It must be strongly emphasized that any measurements on refractory carbides should be accompanied by analyses of gas, oxygen and nitrogen, as well as of carbon contents. The carbon analyser "Avecarbon 100" [29], recently developed at Avesta Jernverks AB of the Axel Johnson Group, Sweden, has been of great value for our investigations. Using this equipment it was possible to measure the carbon content in the samples with an accuracy better than 1% at contents exceeding 0.015% C and better than 0.5% at contents exceeding 0.25% C of a 1 gram sample. A further advantage of this equipment is that very small samples (0.01 g) of carbides, with 6–20 wt.% C, can be analyzed with high accuracy.

This was very important for the carbon analyses of the small gas-carburized filaments [9, 10].

As pointed out the carbides of Group 4b are especially sensitive to gases, which will dissolve in the lattice. Gas analyses of Group 4b carbides is an intricate problem, and it is doubtful if a reliable method exists. However, we have chosen the liquid extraction method with a Pt bath for all our gas analyses. This made it possible to get an approximate idea of the gas contents in samples prepared by different methods. As discussed in refs. [9] and [10] and in the sections above, the gas content of a Group 4b or 5b carbide is dependent on the mode of preparation and was shown to increase in the order: single-crystal growth, arc melting, gas carburization and hot pressing.

Because of the slow diffusion of carbon in transition metals it is very difficult to prepare carbides without composition inhomogeneities. It is therefore important to study the gradients of carbon content by different methods. The hardness and resistivity measurements have been used for this purpose [9, 10]. However, the most accurate analyses for the homogeneity of the carbides are by means of lattice-parameter determinations and a study of the sharpness of the x-ray diffraction patterns [9, 10]. As discussed previously the lattice parameter values may, if properly used together with an accurate carbon analysis, also give an indirect gas analysis. On the other hand, for gasfree carbides the lattice parameter can be used of advantage as an indirect carbon analysis.

ELECTRONIC STRUCTURE OF CARBIDES AND RELATED COMPOUNDS

The unique combination of properties of carbides has led to the development of several models and theories of bonding in these phases. The origin of the cohesion and the electronic structure of carbides have been frequently discussed in the literature since the early forties. The charge distribution between metal and carbon atoms has been especially discussed, although the question of ionicity may be considered tenuous and of little importance if it is considered separately from measurable physical properties.

The following papers are in support of the $Me^{+}C^{-}$ charge distribution: Bilz [30] (1958), Ern and Switendick [31] (1965), Conklin and Silversmith [32] (1968) and Denker [33] (1968). The three first-mentioned papers are quantum-mechanical calculations, ref. [30] using the LCAO-method and refs. [31] and [32] using the APW-method. Ref. [33] describes a model partially based upon quantum-mechanical calculations.

Support for the $Me^{-}C^{+}$ charge distribution is given by the following papers: Umanskij [34] (1943), Robins [35] (1958), Kiessling [36] (1959), Samsonov *et al.* [37] (1953–1966), Dempsey [38] (1963), Engel [39] (1964), Costa and Conte [40] (1964), Surovoy *et al.* [41] (1965), Philipp [42] (1966), Lye *et al.* [43, 44] (1966, 1967), Williams [45] (1966), Storms [12] (1967), Goldschmidt [14] (1967), Holliday [46] (1967) and Fischer and Baun [47] (1968).

Several of the papers in the last group are theoretical considerations and models without any experimental basis. However, three recent, carefully executed experimental investigations [43, 46, 47] supporting a $Me^{-}C^{+}$ charge distribution have been reported. In one of these papers [43] quantum-mechanical calculations (LCAO) based on experimental data are also used. The interpretation of the experimental data reported in two of these papers is discussed in connection with our own measurements in refs. [5] and [7]. The third investigation [47] is discussed in the present paper. It is noteworthy that all the papers supporting a $Me^{+}C^{-}$ distribution are quantum-mechanical calculations, of which those using the Augmented Plane Wave (APW) method [31, 32] so far are the most accurate ones. These calculations have been discussed in detail in connection with our measurements of electron and x-ray spectra.

Electron and x-ray spectra

The electronic structure of transition-metal carbides was studied [5–8] through measurements on the binding-energy shifts of the core-level electrons ($1s$, $2p$, $3d$ and $4f$ electrons), on the $K\alpha_1$, $K\beta_{1,3}$, $L\alpha_{1,2}$ and $L\beta_1$ energy shifts and finally on the K and L emission bands, i.e. the valence electrons. The core-level energies were measured with an iron-free double-focussing ESCA spectrometer [7], the K absorption edges, the $K\alpha_1$, $K\beta_{1,3}$, $L\alpha_{1,2}$ and $L\beta_1$ energies and the emission bands with a 2 meter bent-crystal vacuum spectrometer of Johann type [5].

The electron spectroscopy method, ESCA, which has been developed to a high degree of precision by Siegbahn and coworkers [48], basically implies kinetic-energy analysis of the expelled photo and Auger electrons from a specimen irradiated by monochromatic x-rays, see Fig. 4. Different electronic levels give different kinetic energies of the

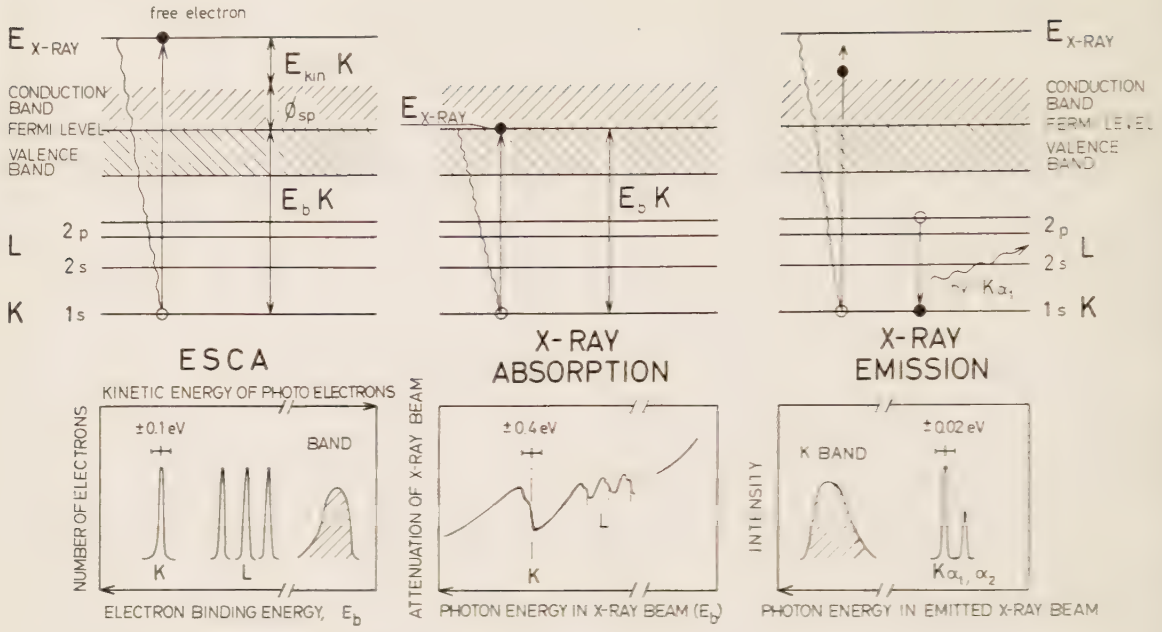

Fig. 4. Atomic processes in a metallic sample for the ESCA, x-ray absorption and x-ray emission methods and their resulting spectra. ● = electron, ○ = vacancy.

measured expelled electrons. For solid specimens the binding energies, E_b, of the electron levels are given by the kinetic energies, E_{kin}, as revealed in the measurements, by the energy of the x-ray radiation, $E_{x\text{-}ray}$, and by the work function of the spectrometer-tank material, ϕ_{sp}; i.e. $E_b = E_{x\text{-}ray} - E_{kin} - \phi_{sp}$. The binding energies are thus related to the Fermi level of the specimen. The high precision of the method makes it possible to study small energy shifts, ~0.1 eV, of the binding energies. Although the core levels are not directly involved in the chemical bonding, they are shifted relative to pure elements in partially ionic compounds [5, 48]. These energy shifts are small compared to the spacings between different levels in the same compound. This implies that a perturbation theory is applicable, and, as discussed by Manne [49], the energy shifts are in the first place attributed to changes in the effective potential due to redistribution of valence electrons. The chemical bonding in a material can thus be studied advantageously by measuring the shifts of the core-electron levels with the ESCA method.

X-ray emission spectra are excited by electron or x-ray bombardment of a sample. As illustrated in Fig. 4, the emission spectra represent the energy transitions which occur when filling the produced inner level vacancies by outer level electrons. For example, the $K\alpha_1$ line represents a filling of a 1*s* vacancy by a $2p_{\frac{3}{2}}$ electron and can be accurately measured, to ±0.02 eV. Studies of the valence band can also be made through the emission spectra; the $K\beta_5$ line in Ti thus represents transitions from the valence band to the 1*s* level.

As can be seen in Fig. 4, x-ray absorption, like the ESCA method, implies a photoelectric effect, and binding energies can be measured by both methods. However, in the x-ray absorption process the bound electron is promoted to allowed unoccupied levels according to relevant selection rules. For carbides the first allowed levels will be in the conduction band at the Fermi level. The structure of higher regions of the conduction band is revealed when the energy of the x-ray beam increases. The structure of the conduction band often complicates the interpretation of the positions of the absorption edges, which for

Table II. *Shifts to lower binding energy of the carbon 1s level in carbides referred to carbon in hydrocarbon (graphite)*

Shift, eV					
Group 4b		Group 5b		Group 6b	
TiC	3.3±0.1	VC	2.6±0.1	Cr_3C_2	2.0±0.1
ZrC	3.7±0.1	NbC	2.9±0.1	Mo_2C	2.1±0.1
HfC	4.0±0.1	TaC	2.9±0.1	WC	2.1±0.1

Table III. *Shifts of the metal 1s, $2p_{3/2}$, $3d_{5/2}$, $4f_{7/2}$ and carbon 1s binding energies and the metal $K\alpha_1$, $L\alpha_{1,2}$ and $L\beta_1$ lines in cubic carbides with varying carbon content relative to pure elements*

Carbide	Shift, eV					
	Ti 1*s*	Ti $2p_{3/2}$	C 1*s*	Ti $K\alpha_1$		
$TiC_{0.97}$	1.0±0.4	1.3 ±0.1	−3.3±0.1	−0.33±0.02		
$TiC_{0.88}$		1.3_5±0.1	−3.3±0.1			
$TiC_{0.78}$		0.9 ±0.1	−3.3±0.1			
$TiC_{0.68}$		0.9_5±0.1	−3.3±0.1	−0.09±0.04		
$TiC_{0.59}$		0.6 ±0.1	−3.3±0.1			
	V 1*s*	V $2p_{3/2}$		V $K\alpha_1$		
$VC_{0.88}$	1.5±0.4	1.8±0.1	−2.6±0.2	−0.21±0.03		
$VC_{0.72}$		1.5±0.1	−2.6±0.2	−0.09±0.03		
		Nb $3d_{5/2}$			Nb $L\alpha_{1,2}$	Nb $L\beta_1$
$NbC_{0.94}$		1.2_4±0.1	−2.9±0.2		0±0.04	0±0.06
$NbC_{0.90}$		1.2_8±0.1	−2.9±0.2		0±0.04	0±0.06
$NbC_{0.77}$		1.4_0±0.1	−3.0±0.2		0±0.04	0±0.06
		Ta $4f_{7/2}$			Ta $L\alpha_{1,2}$	
$TaC_{0.99}$		1.6±0.2	−2.9±0.2		0±0.04	
$TaC_{0.96}$		1.7±0.2	−2.9±0.2		0±0.04	
$TaC_{0.89}$		1.6±0.2	−2.9±0.2			
$TaC_{0.74}$		1.8±0.2	−3.1±0.2			

carbides can be measured to within ±0.4 eV. Often both absorption and emission spectra are used in order to establish the Fermi level, especially when the density of states is low.

In order to study the charge distribution in carbides of Groups 4b, 5b and 6b we measured by the ESCA method the binding energy of the C1*s* level in the carbides and in graphite (vacuum-pump oil). It was found that the binding energy of the C1*s* level is lower in carbides than in graphite, which implies negative carbon atoms in carbides [7]. The C1*s* energy shift is also largest for Group 4b carbides and smallest for Group 6b carbides, see Table II. This is essentially in agreement with Pauling's electronegativity rules.

To obtain additional relevant data we studied the 1*s* and $2p_{\frac{3}{2}}$ level energies of the titanium and vanadium atoms in carbides and in pure metals. The metal binding energies were shown to be higher for the carbides than for the metals, which implies positive metal atoms in these carbides. Measurements on the Ti*K* absorption edges also show higher binding energies for the Ti*K* level in TiC than in the pure metal [5]. The ESCA data show that the metal $2p_{\frac{3}{2}}$ shifts are larger than the metal 1*s* shifts. The differences between the metal $2p_{\frac{3}{2}}$ and 1*s* shifts were found to be in close agreement with the measured Ti$K\alpha_1$ [5] and V$K\alpha_1$ [6], shifts on the same specimens, see Table III. We interpreted [5] these shifts to be a result of the removal of metal 3*d*-electrons using the Hartree–Fock–Slater and Hartree–Fock calculations by Lindgren [50] and Clementi [51] respectively on core level shifts in free atoms with an electron hole in various outer shells. The measured Ti$K\alpha_1$ shift in TiC (−0.33 eV) equals in this interpretation a loss of ~0.4 3*d* electrons. These results are supported by the recent self-consistent Augmented Plane Wave (APW) calculation on TiC by Conklin and Silversmith [32]. As discussed by Conklin and Silversmith the Ti4*s* electrons and probably less than one Ti3*d* electron are transferred to the carbon 2*p* levels in the TiC lattice. It is noteworthy, however, that the spatial charge transfer should be less than one electron for TiC since the Ti4*s* and C2*p* orbitals have their greatest amplitudes in about the same region of space. Bonding in TiC is, according to this calculation [32] and an earlier APW calculation by Ern and Switendick [31], a mixture of covalent Ti3*d*-C2*p* interactions and ionic bonding. This earlier calculation [31] also supports our results regarding the charge transfer in TiC.

Since the variation of physical and chemical properties with carbon content is known to be substantial, a further aim was to study the change in the electronic structure with composition. ESCA and x-ray data for the studied TiC_x, VC_x, NbC_x and TaC_x phases [5–8] are summarized in Table III.

The Ti$2p_{\frac{3}{2}}$ levels were studied for the TiC_x phase and it was found that the $2p_{\frac{3}{2}}$ binding energy increases with increasing carbon content [7]. It was

thus concluded that the ionicity increases with carbon content. To support these electron-spectroscopy measurements we studied the $K\alpha_1$ emission lines for $TiC_{1.0}$ and $TiC_{0.7}$ [5]. An increasing positive charge of the titanium atom implying an increasing ionicity of the bond when carbon atoms are added was found also by these measurements.

The ESCA binding-energy shifts for VC_x of varying composition were shown to resemble those for TiC_x [8]. Only two VC_x samples are reported in Table III but these values have been supported by preliminary ESCA measurements on several VC_x ($x = 0.88 - 0.77$) samples prepared by gas carburization.

The ESCA binding-energy shifts of the Nb $3d_{\frac{5}{2}}$ level showed that the ionicity of the bond increases when *removing* carbon atoms [8]. Studies on the TaC_x phases indicated an analogous behaviour of the bond. However, the interpretation of the measured Ta $4f_{7/2}$ binding-energy shifts was considered somewhat uncertain due to the low binding energy (23 eV) and conceivable mixing with other states in the band [8].

From Table III it is interesting to notice that also the carbon 1*s* shifts suggest an increasing ionicity in the NbC and TaC phases when carbon atoms are removed. For the TiC and VC phases, on the other hand, the C1*s* shift is constant with composition.

In addition to the ESCA measurements, the metal *K* x-ray spectra for the VC_x and *L* spectra for the NbC_x and TaC_x phases were studied. The energy shifts of the V$K\alpha_1$ line in $VC_{0.88}$, $VC_{0.72}$ vs. pure V showed results analogous to those found for the TiC phase, i.e. the negative V$K\alpha_1$ shift increases with increasing carbon content, see Table III. Unfortunately, the $K\alpha_1$ lines of the NbC and TaC phases have too high energies to be measurable with the available x-ray spectrometer [5, 6]. As can be seen in Table III the measured Nb and Ta $L\alpha_{1,2}(M_{V,IV} \rightarrow L_{III}$, $3d_{\frac{5}{2},\frac{3}{2}} \rightarrow 2p_{\frac{3}{2}})$ and Nb$L\beta_1$ $(M_{IV} \rightarrow L_{II}$, $3d_{\frac{3}{2}} \rightarrow 2p_{\frac{1}{2}})$ energies are constant with composition. Within error limits these energies do not exclude an increasing ionicity when carbon atoms are removed, and agree thus with the ESCA shift in these phases. The experimental data thus show that the VC phase qualitatively resembles the TiC, ZrC and HfC phases and consequently differs from the NbC and TaC phases. So far no acceptable explanation to these facts has been given.

In his localized molecular orbital model for cubic refractory compounds, Denker [33] suggests the stability of the phase to be a function of the number of valence electrons. TiC, a Group 4b carbide, with its 8 valence electrons has a stable orbital configuration with only the bonding states, localized around the carbon atoms, occupied, while TaC, a Group 5b carbide, with its 9 valence electrons has a weakened configuration because of partial filling of the anti-bonding levels around the metal cations. Increasing occupancy of the anti-bonding levels thus implies a decreasing ionicity of the bond. Denker's model does not give a complete description of the nature of cubic carbides. However, his model is in partial agreement with the ESCA studies [8], since the ionicity of the NbC and TaC phases decreases when carbon atoms are added.

Although Denker [33], following the APW calculations by Ern and Switendick [31], predicts the ionicity to increase in the order TiC-TiN-TiO, i.e. in accordance with the electronegativity rules, it is evident from his discussion cited above that the additional valence electrons in TiN and TiO start filling the anti-bonding levels and consequently reduce the ionicity of the bond. A balance between increasing electronegativity and filling of anti-bonding levels occurs. Measured Ti$K\alpha_1$ shifts in TiC, TiN and TiO show, in agreement with the Ti1*s* and Ti$2p_{\frac{3}{2}}$ energy shifts, that titanium is most positive in TiC, less so in TiN and TiO, see Table IV. This would imply that the filling of the anti-bonding levels outruns the increasing electronegativity in that order. From the APW calculation on TiC by Conklin and Silversmith [32] it is evident that the anti-bonding levels are mainly Ti3*d* levels, i.e. the occupancy of the Ti3*d* states would increase from TiC and TiN to TiO. A self-consistent APW calculation has quite recently been made also for TiO by Switendick [5a]. This calculation shows, in agreement with our interpretation of the experimental data and in disagreement with the previous theories [31] and [33], somewhat higher occupancy of the Ti3*d* states in TiO compared to TiC. The difference of ~0.15 Ti3*d*-electrons given by the self-consistent APW calculations [5a, 32] is in fairly good agreement with our interpretation based on Hartree–Fock calculations of free atoms and ions [5]. The measured differences in the Ti$K\alpha_1$ and ESCA (Ti$2p_{\frac{3}{2}}$ − Ti1*s*) energy shifts for the TiC and TiO phases correspond in this interpretation to a difference of ~0.30 Ti3*d* electrons.

Information about the band structure was obtained from measurements of the Ti*K* emission bands

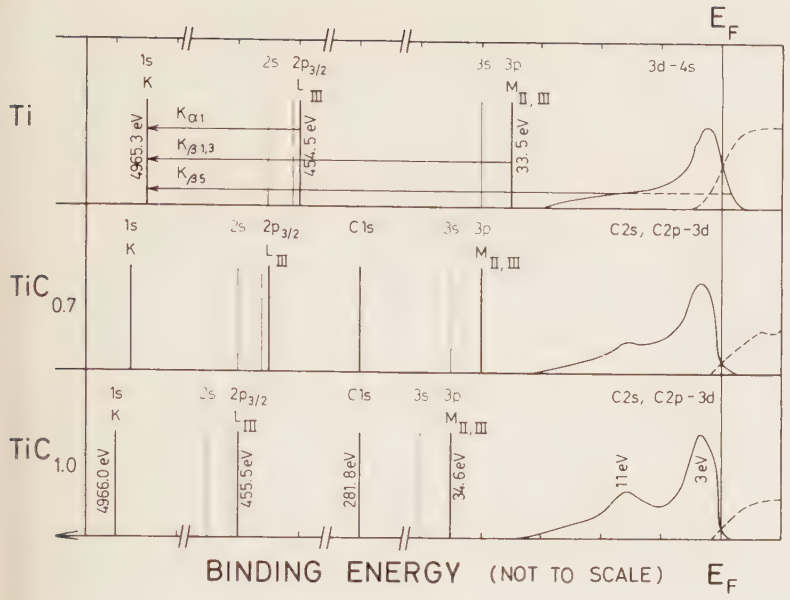

Fig. 5. Electronic structures of Ti, $TiC_{0.7}$ and $TiC_{1.0}$ constructed from electron and x-ray spectra. E_F represents the Fermi level. The binding energies given for the TiC phase are approximative and based upon the energies for Ti taken from J. A. Bearden and A. F. Burr, Atomic energy levels, U.S. Atomic Energy Commission, NYO-2543-1, Oak Ridge, Tenn., USA, 1965.

for Ti, $TiC_{1.0}$, $TiC_{0.7}$, TiN, TiO and TiB_2. It was found that the density of states at the Fermi level was low for TiC and somewhat increasing for TiN and TiO. As pointed out in ref. [5] this is in agreement with the density of states as calculated by the APW method [5a, 32]. From the interpretation of the $K\alpha_1$-shift measurements and from the APW calculations [5a, 32] it could be concluded that the increase of the density of states at the Fermi level in the TiN and TiO phases compared to the TiC phase is due to the increasing occupancy of the Ti3*d* orbitals.

It is interesting to notice that our measurements and the APW calculations on TiC show no gap between the valence and the conduction bands. In agreement with the band calculations by Altmann and Bradley [52] a much higher density of states was found for the pure Ti metal in contrast to the TiC, TiN and TiO phases. The density of states for $TiC_{0.7}$ was found to be lower than that for $TiC_{1.0}$, mainly due to emptying of the C2*s* levels. That the valence band of TiC contains C2*s* and C2*p*-Ti3*d* states emerges from the quantum-mechanical calculation [32] previously mentioned and from a comparison between Holliday's [46] C*K* emission band, fit to the Fermi level with the ESCA C1*s* peak, and our Ti*K* emission band. See Fig. 4 in ref. [5].

The electronic structures of $TiC_{1.0}$ and $TiC_{0.7}$ relative to pure Ti are illustrated in Fig. 5. Measured electron levels and transitions are printed in a fat bold-face type. The levels and transitions measured in x-ray absorption and emission are denoted *K*, *L* and *M*, while 1 and 2 are used for the levels measured by ESCA. The band structure measured by x-ray spectroscopy is marked with figures.

The V*K* emission bands were measured for V, $VC_{0.88}$ and $VC_{0.72}$ [6]. The densities of states for VC_x were found to be low at the Fermi level and resemble those for TiC_x. The high energy peak corresponds consequently to the C2*p*-V3*d* levels and the low energy peak to the C2*s* levels. This low energy peak was not found in the $L_{II,III}$ emission spectra for the NbC_x and ZrC phases [6]. Binding-energy shifts are more accurately studied by measuring the core-level shifts than by measuring the emission-band shifts. However, the band shifts measured for the VC_x, NbC_x and ZrC phases relative to the pure metals show that the metal atoms are positive in the carbides.

To compare the carbides with other refractory compounds we studied the Ti2$p_{\frac{3}{2}}$, non-metal 1*s*, Ti$K\alpha_1$ and Ti*K* absorption-edge energy shifts in TiB_2 and TiO_2, see Table IV, beside the previously mentioned TiN and TiO. We found that the metal atoms were positive for all materials studied. However, the results for TiB_2 were found to be somewhat inconclusive. Judging from the most accurate measurements, i.e. the $K\alpha_1$ line, supported by the ESCA measurements on the Ti2$p_{\frac{3}{2}}$ energy shift, the titanium atoms are donating electrons to the non-metal atoms also in that phase.

Some recent soft-x-ray investigations have been

Table IV. *Shifts of the metal K absorption edge, metal 1s and $2p_{3/2}$ binding energies and $K\alpha_1$ line in titanium boride, carbide, nitride and oxides relative to titanium metal*

Compound	Shift, eV			
	Ti*K*	Ti 1*s*	Ti $2p_{3/2}$	Ti $K\alpha_1$
TiB_2	-0.5 ± 0.4		0.3 ± 0.2	-0.18 ± 0.04
TiC	0.7 ± 0.4	1.0 ± 0.4	1.3 ± 0.1	-0.33 ± 0.02
TiN	1.8 ± 0.3	1.2 ± 0.4	1.5 ± 0.2	-0.19 ± 0.04
TiO	0.5 ± 0.3	1.0 ± 0.4	1.0 ± 0.2	-0.09 ± 0.03
TiO_2		4.3 ± 0.4	4.9 ± 0.2	

interpreted to show charge transfer in carbides which are in contrast to the results presented here. The discrepancies are generally connected to measurements on the emission bands and absorption edges. Due to the difficulties involved in interpreting the shifts of these bands and edges a wrong result may be given.

The difficulty in finding the Fermi level in emission bands when the density of states is low is illustrated in ref. [7] by comparing the C*K*, Ti and V$L_{II,III}$ x-ray emission bands by Holliday [46] with the corresponding ESCA energies of C, Ti, V, TiC and VC. In his paper on metal $L_{II,III}$ and carbon *K* emission bands of metallic carbides, Holliday [46] evaluated the shifts of the bands in such a way that he concluded the metal atoms to be more negative in the carbides than in the pure metals. However, if the shifts of Holliday's emission bands are measured relative to the Fermi level and not relative to the band-structure dependent maxima of the peaks, i.e. if measurements are performed in the way we proposed in ref. [7], his experimental data perfectly fit our picture of the electronic structure of carbides.

The same criticism regarding the interpretation of the shifts of the emission bands applies to the investigation by Fischer and Baun [47] on the titanium $L_{II,III}$ x-ray emission and absorption spectra from titanium metal, oxides, nitride, carbide and boride. Their results indicate a charge transfer in TiC which is in contrast to that in TiB_2, TiN and Ti oxides. Fischer and Baun state, however, that the absorption spectrum from the carbide was quite difficult to obtain. As is clear from a comparison of our own ESCA and x-ray work, ESCA is the more accurate method for measuring binding energies. Our ESCA measurements on the Ti2*p* ($L_{II,III}$) binding energies in Ti and TiC_x are in contrast to Fischer and Baun's results. One possible explanation to this discrepancy between their absorption and our ESCA data would be that their TiC sample was contaminated or ill-defined. In contrast to their detailed description of the spectrometer and measuring method used, no relevant data are given for the test sample.

Concluding remarks on the studies on the electronic structure

As is evident from our papers [5–8] and the sections above, the electronic structure of transition-metal carbides could be elucidated owing to a number of conspiring circumstances. The recently developed ESCA method makes it possible to measure the electron levels and their shifts in solids with high precision. This method could be applied successfully to carbides, since these were shown to exhibit well-defined surfaces, representative of the intrinsic material properties. Furthermore, the progress of energy-band theory has reached the point where fairly accurate calculations are being made on transition metals and their compounds. The first self-consistent APW calculations on TiC [32] and TiO [5a] were thus made simultaneously with our measurements on the electronic structure of these compounds. Finally, the progress within the theoretical field together with the ESCA data made it possible to interpret more exactly the x-ray absorption and emission spectra of transition-metal compounds.

The electronic structure of transition-metal carbides as revealed by electron spectroscopy and x-ray absorption and emission measurements interpreted with Hartree–Fock–Slater and Hartree–Fock calculations on free atoms and ions [5, 50, 51] and supported by the self-consistent APW calculation on TiC by Conklin and Silversmith [32] may be summarized as follows.

1. In transition-metal carbides the metal atoms are positive and the non-metal atoms negative (Me^+C^-), i.e. an ionic bond is present.

2. For TiC the occupancy of the 4*s* and 3*d* states are less in the carbide than in the metal. The spatial charge distribution is mainly due to the Ti3*d* electrons, which are transferred to the C2*p* states. It appears safe to conclude that for other metal carbides the metal atoms also lose *d* electrons to the C2*p* levels.

3. The bonding in TiC is also caused by interactions between the Ti3*d*, Ti4*s* and C2*p* levels, where the Ti4*s* orbitals, however, contribute negligibly to

the occupied states in the solid. This hybridized *p–d* function probably exists for other carbides too.

4. The ionicity in TiC_x, ZrC_x, HfC_x and VC_x increases when carbon atoms are added, while the inverse is true for the bonding in NbC_x and TaC_x.

5. The metal atoms in the series TiC-TiN-TiO are positively charged and the electronic transfer is largest for carbides, less for nitrides and oxides; the occupancy of the Ti3*d* states increasing in that order. TiB_2 and TiO_2 also have positively charged metal atoms due to a loss of Ti3*d* electrons.

PHYSICAL AND CHEMICAL PROPERTIES RELATED TO THE ELECTRONIC STRUCTURE

We will now discuss more in detail how heat of formation, lattice parameter, hardness, wetting angle and resistivity of stoichiometric and non-stoichiometric carbides can be understood and qualitatively explained through the model of the electronic structure put forward. But before entering this discussion it is of importance to define more in detail the meaning of the energy shifts of the core-level electrons (ESCA shifts) and how these shifts are correlated to the ionicity and to the electrostatic energy of the carbide lattice.

Ionic contribution to cohesion and ESCA shifts. The electrostatic (Madelung) energy of cubic carbides

The electrostatic energy, I, of an ionic lattice is given by the coulombic interactions among the ions. The potential energy varies inversely with the first power of R_{ij}, the interionic distances, i.e.

$$I = \sum_{i<j} \frac{q_i q_j}{R_{ij}} = \tfrac{1}{2} \sum_i \sum_{j \neq i} \frac{q_i q_j}{R_{ij}} \tag{1}$$

where q_i and q_j are the effective charges of the ions.

For the ith atom, we have

$$I_i = \tfrac{1}{2} q_i \sum_{j \neq i} \frac{q_j}{R_{ij}}, \quad \text{and} \quad I = \sum I_i \tag{2}$$

In the cubic carbide structure (B1, NaCl) the electrostatic energy per unit cell, I_e, can be divided into two terms, one for each atom.

$$I_e = I_+ + I_- = \tfrac{1}{2} q_+ \sum_{j \neq +} \frac{q_j}{R_{+j}} + \tfrac{1}{2} q_- \sum_{j \neq -} \frac{q_j}{R_{-j}} \tag{3}$$

where the symmetry gives $I_+ = I_-$ and $q_+ = -q_- = q$, i.e.

$$I_e = q_+ \sum_{j \neq +} \frac{q_j}{R_{+j}} \tag{4}$$

This equation may be rewritten in the form

$$I_e = -\frac{q^2 \cdot \alpha}{R} \tag{5}$$

where α is the Madelung constant, dimensionless and dependent upon the arrangement of positive and negative ions in the lattice. $\alpha_R = 1.7476$ for the NaCl structure. Here we use for convenience the Hartree system of atomic units, i.e. I_e is given in Hartrees: 1 H = 27.21 eV and R is given in Bohr radii: 1 B = 0.52918 Å and q is the effective atomic charge given in numbers of electrons. The Madelung energy, I_e, tends to collapse the lattice, which, however, does not occur, because there are repulsion terms of quantum-mechanical nature. Generally the Madelung energy is much larger than the repulsion energy which implies, at least in a qualitative discussion, that the total ionic contribution to cohesion of a mole carbide may be approximated to

$$I_E \approx \frac{q^2 \cdot \alpha \cdot N}{R} \tag{6}$$

where N = Avogadro's number. Provided that the ESCA shifts, S, are measured relative to vacuum and that only electrostatic interactions are of importance for the shifts we can write [48]

$$S_i = q_i \gamma_i + \sum_{j \neq i} \frac{q_j}{R_{ij}}; \quad S = \pm q\left(\gamma - \frac{\alpha}{R}\right) \tag{7}$$

where γ represents the Coulomb repulsion between the charge q and the core electron on the same atom. The second term is the electrostatic energy from the rest of the crystal as discussed above.

Combining (5) and (7) gives

$$I = \frac{S^2}{\left(\gamma - \frac{\alpha}{R}\right)^2} \cdot \frac{\alpha}{R} \tag{8}$$

With the lattice parameter and ESCA shifts experimentally determined and the charge q for TiC estimated to be 0.4 from the $K\alpha_1$ emission and ESCA Ti2$p_{\frac{3}{2}}$ and Ti1*s* energies, we get from Eq. (7) $\gamma_{C1s} = 0.73$ Hartree.

γ_{C1s} can also be given by quantum-mechanical calculations on free ions.

Table V. *Electrostatic energies calculated from ESCA carbon 1s binding energy shifts and heats of formation for cubic carbides of Groups 4b and 5b*

Carbide	ESCA shift S, $-\Delta C1s$, eV	Atomic charge q $\pm e$	Interionic distance R B radii	Electrostatic energy $-I_E$ kJ/mole	Heat of formation $-\Delta H_{298°K}$ kJ/mole
TiC	3.3	0.40	4.090	179	184
ZrC	3.7	0.45	4.439	209	197
HfC	4.0	0.48	4.384	241	209
VC	2.6	0.32	3.936	117	103
NbC	2.9	0.35	4.223	132	140
TaC	2.9	0.35	4.210	133	143

From a study of the C1*s* shift in various free-ion calculations by Lindgren [50] and Clementi [51] one gets $\gamma_{C1s} = 0.60$ Hartree [53]. A direct calculation of the Coulomb repulsion integral using Clementi's wave-function for the carbon atomic ground state gives $\gamma_{C1s} = 0.78$ Hartree [53]. The latter method usually gives larger values than the former, where the other valence electrons have the opportunity to compensate for the loss or addition of a valence electron. Both estimates are made under the assumption that the valence orbital involved is a $2p$ orbital.

For the 4b and 5b cubic carbides the lattice parameter varies from 4.166 Å (VC) to 4.698 Å (ZrC) and R from 3.936 to 4.439 B respectively. The term α/R consequently varies from 0.444 to 0.394 H which implies that S in Eq. (7) varies ~ 15% from this term. This variation may be considered small compared to the one-center term in a qualitative discussion, i.e. $\alpha/R = C$ for Group 4b and 5b cubic carbides. Eqs. (7) and (8) may then be written in the forms

$$S = C' \cdot q \tag{9}$$

and

$$I = -\frac{S^2}{R} \cdot C'' \tag{10}$$

where C, C' and C'' are constants. In this approximation the ESCA shift is a direct measure of the charge transfer, and the electrostatic energy in the carbide is proportional to the square of the ESCA shifts divided by the interionic distance. For the cubic carbides of Groups 4b and 5b S is a monotonic function of S^2/R, which implies that the ESCA shift may be used as a measure of the electrostatic energy in these phases.

With the charge $q = 0.4$ for TiC, we can calculate the Madelung energy, Eq. (6), and obtain –179 kJ/mole TiC. Using the data for TiC we can estimate the charge, q, for the other cubic carbides of Groups 4b and 5b and calculate their electrostatic energies. These are given in Table V together with the heats of formation of the carbides. Though the carbides in many ways differ from ionic crystals it is amazing to note that this simple estimate gives such a good relationship between these two quantities. The increased stability of carbides over the elements in solid form evidently equals the electrostatic contribution to bonding.

Heat of formation

From the survey by Storms [12] we know that the heats of formation of stoichiometric carbides increase from Group 6b to Group 4b. It is interesting to note that the measured C1*s* binding-energy shifts of stoichiometric or nearly stoichiometric carbides of Groups 4b, 5b and 6b can be related to their heats of formation, see Fig. 6, i.e. in agreement with the theoretical considerations made in the previous section.

The proposed electronic structure and its variation with carbon content must also be able to explain the variations of heats of formation within the homogeneity ranges of the cubic carbides of Groups 4b and 5b. The heat of formation per atom, and thus the bond strength, increases with increasing carbon content for the TiC, ZrC and VC phases and is constant or decreasing for the NbC and TaC phases. This is in excellent agreement with the ESCA shifts [7, 8] given in Table III. These qualitative relationships are illustrated in Fig. 7. It should be noticed that only preliminary ESCA measurements have been made on the ZrC and HfC phases. Therefore these phases are put in brackets in Fig. 7 (and in Fig. 9). The linear relationships in Figs. 6 and 7 show that the ESCA shifts may be used as a measure of bond strength in

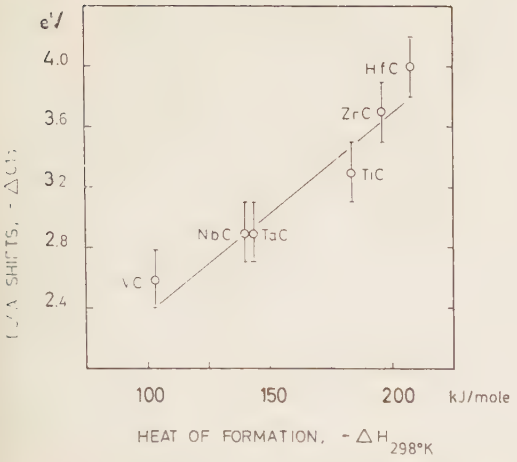

Fig. 6. Relationship between ESCA carbon 1*s* binding energy shifts and heats of formation for cubic carbides of Groups 4b and 5b.

a cubic carbide. Furthermore, the linear relationships are strongly suggestive that the variations in bonding between various carbides and with composition in one given carbide are mainly ionic vis-a-vis covalent.

Lattice parameter

As discussed previously the lattice parameter curves of Group 4b carbides exhibit a maximum. For Group 5b carbides, on the other hand, the lattice parameter increases with increasing carbon content. A qualitative explanation for this behaviour can be made as follows. Two different forces affect the carbide lattice. One force is attributed to the geometrical space demand for the carbon atoms, i.e. the

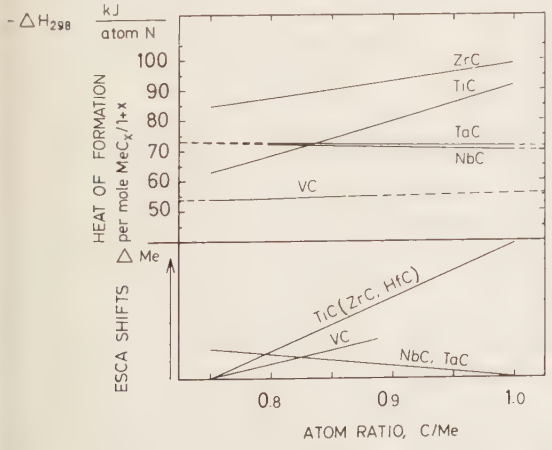

Fig. 7. Relationships between ESCA metal binding energy shifts and heats of formation per mole $MeC_x/(1+x)$ as functions of carbon content of cubic carbides of Groups 4b and 5b.

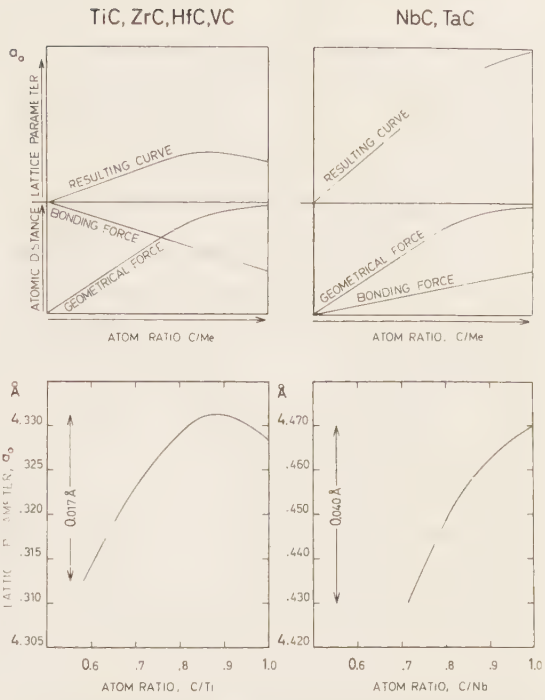

Fig. 8. Theoretically predicted and measured relationships between lattice parameter and carbon content of TiC, ZrC, HfC and VC versus NbC and TaC.

lattice will expand when carbon atoms are added to the octahedral voids. The other force is the bonding force. For the TiC, ZrC, HfC and VC phases the bond strength increases with increasing carbon content, for the NbC and TaC phases the inverse is valid. This implies that the lattice parameter values for the two latter phases should increase substantially when carbon atoms are added, since both the geometrical and the bonding forces are cooperating in expanding the lattice. This is illustrated in Fig. 8, where theoretically predicted and measured lattice parameter curves are shown. For the TiC, ZrC, HfC and VC phases these two forces will counteract each other and, as we discussed in ref. [10] and as illustrated in Fig. 8, may possibly give rise to a maximum similar to that experimentally observed. Notice that the narrow homogeneity range of VC hinders the occurrence of a maximum for this phase.

As discussed the lattice parameters of Group 4b carbides are lowered by dissolved oxygen and nitrogen. This implies a stronger bond when small amounts of oxygen and nitrogen are added. According to Denker [33] maximum bond strength occurs at a valence-electron concentration of $\gtrsim 8$, i.e. a TiC_xO_y where $x<1$ and $y \leqslant 1$ would have optimum stability.

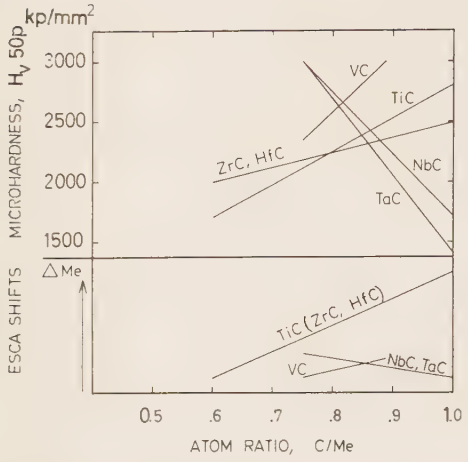

Fig. 9. Relationships between ESCA metal binding energy shifts and hardness as functions of carbon content of cubic carbides of Groups 4b and 5b.

The deviations from the linear relationship between Ti2$p_{\frac{3}{2}}$ shifts and carbon content in TiC found from the measurements on the TiC_x phases ($x = 0.6$–1.0), see Fig. 4 and Table I in ref. [7], suggest that increasing oxygen content (0.08–0.31 wt.%) increases the Ti2$p_{\frac{3}{2}}$ energy shift, i.e. the bond is increased due to increasing ionic contribution. It is important to notice that high contents of oxygen, i.e. in TiO, weaken the bonding relative to carbon, i.e. in TiC, due to filling of the Ti3*d* anti-bonding states as discussed above. According to Storms [12], dissolved gases raise the lattice parameter of Group 5b carbides. Using Denker's [33] model one predicts the lattice parameter of VC, NbC and TaC to be raised by oxygen, since the additional electrons in oxygen compared to carbon bring the valence-electron concentration still further from the optimum bond strength at $\gtrsim 8$ valence electrons. However, since we have found the variation of bond strength with carbon content in VC to differ from that in NbC and TaC one can suspect the influence of small amounts of oxygen to be different in the three phases. The VC phase may thus resemble a Group 4b phase also in this respect. However, the effect of dissolved gases on the bond strength has so far not been studied enough in our investigations. Without doubt, an investigation based on the use of the ESCA method would lead to a better understanding of the influence of dissolved gases on the properties of refractory compounds.

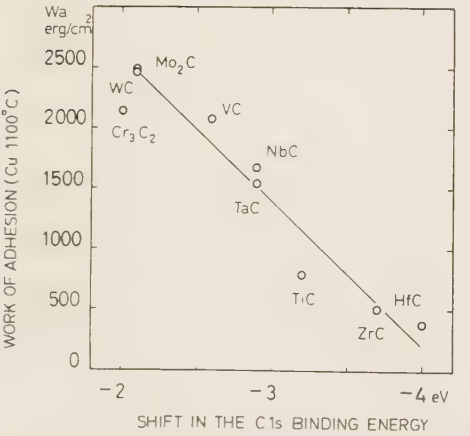

Fig. 10. Relationship between works of adhesion (Cu 1100°C) and ESCA carbon 1*s* binding energy shifts of carbides of Groups 4b, 5b and 6b.

Hardness

We have previously discussed that the hardness increases when carbon atoms are added within the composition ranges of the TiC, ZrC, HfC and VC phases. For the NbC and TaC phases the inverse is valid. As has been shown experimentally the bond strength varies with carbon content in a similar way. The qualitative relationships between the ESCA metal shifts and the hardness for cubic carbides of Groups 4b and 5b with varying carbon content are illustrated in Fig. 9. Through the ESCA measurements we can thus understand and qualitatively explain the variations of the hardness with carbon content. Small amounts of dissolved gases were found to raise the hardness of Group 4b carbides. This behaviour is analogous to that discussed above for the lattice parameter.

Wetting by liquid metals

We know that both wetting angles or works of adhesion and ESCA shifts can be related to the heats of formation of stoichiometric and non-stoichiometric carbides. The wetting angles or works of adhesion can thus be related to the core-level energy shifts. This relationship between works of adhesion and C1*s* energy shifts is shown in Fig. 10. It is obvious that the wetting decreases when the C1*s* energy shift increases, i.e. when the ionicity of the carbide bond increases. Increasing C1*s* energy shifts imply, beside an increasing ionicity, that the metal *d* electrons enter the C2*p* levels and thereby strengthen the inner carbide bond due to *d*-2*p* interactions as discussed above in this paper. The electrons in such a stable configuration may thus have little affinity to interact

with external electrons and consequently a weak bond and poor wetting occur.

Resistivity

The transition-metal carbides of Groups 4b, 5b, and 6b are good conductors of electricity. The quantum-mechanical APW calculations on TiC [31, 32] and our measurements on cubic carbides [5–7] give a low density of states at the Fermi level but no gap between the valence and conduction bands. The carbides would consequently be conductors of electricity, although less good than the corresponding pure metals, i.e. in agreement with our resistivity data reported in ref. [9] and Table I in the present paper.

The resistivity increases when carbon atoms are removed [9, 10] within the homogeneity ranges of the cubic carbides of Groups 4b and 5b. This is also in agreement with the measured densities of states for TiC, VC and NbC which decrease when carbon atoms are removed [5, 6]. This implies less probability that electrons enter the conduction band.

CONCLUSIONS

The refractory carbides of Groups 4b, 5b and 6b prepared by means of hot pressing, gas carburization, arc melting and single-crystal growth have been studied with regard to their physical and chemical properties and electronic structure.

The mode of preparation was found to be of fundamental importance for the intrinsic properties of transition-metal carbides. The carbon content and the distribution of the carbon atoms together with dissolved gases, mainly oxygen and nitrogen, most seriously affect the physical and chemical properties of carbides.

Older property data reported in the literature should be used with care since in the light of present technology it is evident that many of these data apply to measurements on impure and ill-defined test samples. Consequently, important data must be remeasured on well-defined carbides.

New data have been given for hardness, lattice parameter, resistivity and wetting by liquid metals of carbides of Groups 4b, 5b and 6b, and the variations of these properties with composition were especially studied for Group 4b and 5b cubic carbides.

Electron spectroscopy and x-ray absorption and emission measurements on well-defined test samples show that the charge distribution in transition-metal carbides of Groups 4b, 5b and 6b is such that the metal atoms are positive and the carbon atoms negative. Interpretation of the experimental data by means of Hartree–Fock and Hartree–Fock–Slater calculations on free atoms and ions show that the metal atoms lose d electrons. These results are supported by recent self-consistent Augmented Plane Wave calculations on TiC, which show that the electron transfer consists mainly of Ti3d electrons which are going into carbon 2p levels. Thus bonding in carbides is a mixture of ionic bonding and interactions between the metal d and carbon 2p levels.

Experiments as well as simple calculations presented here indicate that the electrostatic lattice energy gives the main contribution to the additional bonding in carbides over the pure elements in solid form. The ionic bonding increases from Group 6b to Group 4b carbides, which is consistent with Pauling's electronegativity rules.

In agreement with the Augmented Plane Wave calculations it was experimentally shown for the cubic carbides that the density of states at the Fermi level is low compared to the pure metals. No gap exists between the valence and conduction bands. The valence band consists mainly of carbon 2s and 2p states, of which the latter interact with metal d levels. The density of states near the Fermi level consequently lowers with decreasing carbon content.

It was shown that ionicity and bond strength increase with increasing carbon content within the homogeneity ranges of the TiC, ZrC, HfC and VC phases. In the NbC and TaC phases, on the other hand, the inverse is valid. These results, showing that the VC phase resembles the Group 4b carbides, correlate well with the variations of recently measured physical and chemical properties with composition of the cubic carbides. These include variations of heat of formation, hardness, lattice parameter, resistivity and wetting by liquid metals.

Studies on TiB_2, TiN, TiO and TiO_2 give results analogous to TiC. For the cubic phases it was found that titanium is most positive in TiC, less so in TiN and TiO; the occupancy of the Ti3d states increasing in that order. It seems likely that the non-metal atoms always are negative in interstitial compounds like transition-metal borides, carbides, nitrides and oxides, and that the metal atoms lose mainly d electrons. Theoretical support for this statement is given by self-consistent Augmented Plane Wave calculations for TiC and TiO.

Additional ESCA measurements on Group 6b borides and 8b corbides are in progress.

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